

Non-isothermal Dehydration Kinetics of Titania Gel

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Abstract

Titania gel was synthesized by sol-gel method and dehydration kinetics of the gel was studied using a thermogravimetric analyzer in the temperature range of 35-700°C at three different heating rates. Dehydration of the gel was observed to take place at two different stages. Kinetic analysis for dehydration at both stages were performed by Friedman model fitting and Kissinger –Akahira –Sunose (KAS) model free methods to determine kinetic triplet. It was observed that dehydration of the titania gel sample followed second order reaction kinetics in both the stages.

Keywords

Sol-gel Process; Dehydration Kinetics; Activation Energy; Friedman Method; Kissinger-Akahira-Sunose a Pproximation

Introduction

Thermogravimetric analysis (TG) is a widely accepted method to study the course of solid state reactions. In non-isothermal analysis, the mass loss of a sample at different heating temperature is measured with controlled heating rate. From the thermogravimetric curves, the kinetic parameters can be calculated since the shape of these curves depend on the reaction kinetics followed at these stages. So to determine the kinetic parameters several model fitting, (where a reaction model is chosen) and model free (where no reaction model is chosen) kinetic calculation methods were developed. Friedman and Kissinger-Akahira-Sunose (KAS) method are the examples of model-fitting and model-free kinetic calculation procedures respectively.

Sol-gel process is one of the most advanced methods for the synthesis of precursor powder for ceramics as it

results in the development of products with relatively higher purity and homogeneity compared to other conventional procedures. During the dehydration of gel water and other volatiles are removed leaving behind the solid residues. A number of works have been reported on the dehydration kinetics of synthetic gels based on thermogravimetric analysis and some of the reported works have been mentioned here. Hernandez-Escolano et al. (2012) performed TG analysis of a gel sample and used model free integral is oconversional non-isothermal procedure for kinetic study. The n=6 kinetic model was observed to be the best fitted for all the system during kinetic model determination by applying Coats-Refern method. Biedunkiewicz et al. (2010) performed TG-DSC measurements under non-isothermal and isothermal conditions at four different temperatures and used Coats-Redfern method to describe the kinetic parameters. Maitra et al. (2008) synthesized zeolite gel and showed that gel dehydration followed first order kinetics and it proceeded through low energy diffusion controlled process. Budrugaec et al. (2007) studied non-isothermal kinetics of decomposition of zinc-acetate based gel precursors using thermogravimetric data. Invariant kinetic parameter (IKP) method was used by the authors for the evaluation of activation energy, pre exponential factor and kinetic model. It was observed that decomposition of the gel sample followed F1 kinetic model. Want et al. (2007) performed thermogravimetric and differential thermal analysis of gel of ytterbium tartrate hydrate. They observed that the decomposition of the gel was started after 200°C and completed in two stages at around 700°C. By using the integral method and

applying the Coats-Redfern approximation, the non-isothermal kinetics parameters like activation energy and frequency factors were evaluated. Jankovic et al. (2005) studied the dehydration process of swollen polyhydrogel at different heating rates. Under non-isothermal condition, different kinetic parameters like activation energy, pre-exponential factor and kinetic model for the hydrogel dehydration process were studied. The results obtained by applying methods like Kissinger, Coats-Redfern etc. under the same heating rates were in good agreement with each other.

In this present investigation, thermogravimetric analysis of titania gel was performed at three different heating rates. The kinetic triplet (reaction order, activation energy and frequency factor) were calculated using Friedman method and the results were further verified by Kissinger-Akahira-Sunose (KAS) approximation method.

Experimental Methods

Synthesis of Stable Titania Gel

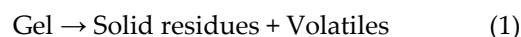
7.08 gm of Potassium Titanium Oxalate [$K_2TiO(C_2O_4)_2 \cdot 2H_2O$ (LOBA CHEMIE, INDIA)] was mix with 200ml of distil water to make 0.1 M KTO solution. To this solution (1:1) (volume /volume ratio) NH_4OH was added till the precipitation was complete. At around pH-12, precipitation was found complete and it was washed thoroughly with distilled water till pH-7. The precipitate was filtered and finally dissolved in (1:1) solution of 30% Hydrogen peroxide (MERCK, INDIA). It was observed that the maximum concentration of TiO_2 would be achieved by the addition of 32 ml solution of H_2O_2 . Thereupon, the total solution was kept at rest for 15-20 min so to dissolve the precipitate completely. To the solution Diethanolamine $C_4H_{11}NO_2$ (DEA) (MERCK, INDIA) was added dropwise till the pH of the solution reached to ~10.

After complete addition of DEA, a stable sol was formed and the sol was dried at 110°C overnight. The dried gel was subjected to TGA study at three different temperatures i.e. 4, 7 and 10°C/min using Perkin Elmer, Pyris Diamond 480. Fourier Transform Infrared studies of per titanic acid and the gel heat treated at five different temperatures (110, 220, 330, 440 and 550°C) were performed using IRPrestige-21, Shimadzu, Japan. X-ray diffraction (XRD) pattern of the gel was taken by Rigaku Ultima III, Japan.

Isoconversional Kinetic Calculations

Dehydration of the gel can be represented by the

following reaction scheme:



The fraction of dehydrated mass ' α ' can be defined by the following expression:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (2)$$

Where m_0 is the mass of the gel at the beginning, m_t and m_f are refer to the masses at time ' t ' and at the end of the experiment respectively.

Rate of dehydration ($\frac{d\alpha}{dt}$), is a linear function of temperature-dependent rate constant, k , and reaction model (a temperature independent function of conversion), $f(\alpha)$:

$$\frac{d\alpha}{dt} = k f(\alpha) \quad (3)$$

Vyazovkin et al. (2011) Studied Isoconversional calculation methods by splitting it into two different categories: differential and integral.

Differential Isoconversional Methods

Replacing the rate constant with Arrhenius equation ($k = A.e^{-\frac{E}{RT}}$), above equation becomes:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} f(\alpha) \quad (4)$$

Where A is the pre-exponential factor, E is the activation energy, R is the universal gas constant and T is the absolute temperature.

By taking the logarithm of equation (3), we can get,

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[A.f(\alpha)] - \frac{E}{RT} \quad (5)$$

This equation was proposed by Friedman as Vyazovkin et al. (2011) By introducing heating rate ($\beta = \frac{dT}{dt}$) in the above equation and rearranging,

$$\ln\left(\frac{d\alpha}{dT}\right) - \ln[f(\alpha)] = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT} \quad (6)$$

The plot of $\ln\left(\frac{d\alpha}{dT}\right) - \ln[f(\alpha)]$ versus $\frac{1}{T}$ would give a straight line. The slope and intercept of the straight line provided the values of activation energy and frequency factor respectively. Values of $f(\alpha)$ were chosen arbitrarily from the Velyana et al. (2013) and

$\ln(\frac{d\alpha}{dT}) - \ln[f(\alpha)]$ values were plotted against $\frac{1}{T}$ and from these plots the best fit value of $f(\alpha)$ was chosen which showed the best correlation coefficient. Now from the plot of best fitted ' $f(\alpha)$ ' value, activation energy and pre-exponential factor were calculated by taking slope = $-\frac{E}{R}$ and intercept = $\ln(\frac{A}{\beta})$ at all the heating rates.

Integral Isoconversional Methods

Integration of equation (3) will give the following form Vyazovkin et al. (2011),

$$g(\alpha) \equiv \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{\left(-\frac{E}{RT}\right)} dT \quad (7)$$

To get a solution of equation (7), several approximations were proposed. Kissinger-Akahira-Sunose (KAS) developed one of such approximation and their proposed equation is the following,

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{AR}{g(\alpha).E}\right] - \frac{E}{RT} \quad (8)$$

Where $g(\alpha)$ is the reaction model which depends on the conversion mechanism and its algebraic expression. For a known reaction model and each degree of conversion (α), the plot of $\ln\left(\frac{\beta}{T^2}\right)$ versus $\frac{1}{T}$ will be a straight line whose slope and intercept can provide the values of activation energy (E) and $\ln\left[\frac{AR}{g(\alpha).E}\right]$ respectively.

To determine the reaction order, the equation (8) has been rearranged in the following way,

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT} \quad (9)$$

Now the plot of $\ln\left[\frac{g(\alpha)}{T^2}\right]$ versus $1/T$ would be a straight line with slope equal to -1.0000 . Using linear regressive of least square method and choosing arbitrary values of $g(\alpha)$ available in the literature [4], $\ln[g(\alpha)/T^2]$ values were plotted against $1/T$ and plot having slope closet to -1.0000 and correlation coefficient closet to unity was considered as the best fit mechanism function of $[g(\alpha)]$.

Subsets of the TG-curves at certain values of α and corresponding temperatures were taken and the dependence of $\ln[\beta/T^2]$ on $1/T$ was drawn according to

equation (8) for both stages. The activation energy E and frequency factor were determined from the slope and intercept of each plot using equation (8).

Result and Discussion

When ammonium hydroxide was added to the solution of potassium titanium oxalate, basic titanium hydroxide $[\text{TiO}(\text{OH})_2]$ was precipitated. The precipitate was dissolved by the addition of hydrogen peroxide as Ti^{4+} and H_2O_2 interact strongly and form peroxotitanic acid as Myers et al. (2004), To this solution DEA was added to form the stable sol. The solution became hot during the addition of DEA indicating exothermic nature of the reaction.

The FTIR spectra of the samples have been shown in the Fig. 1.

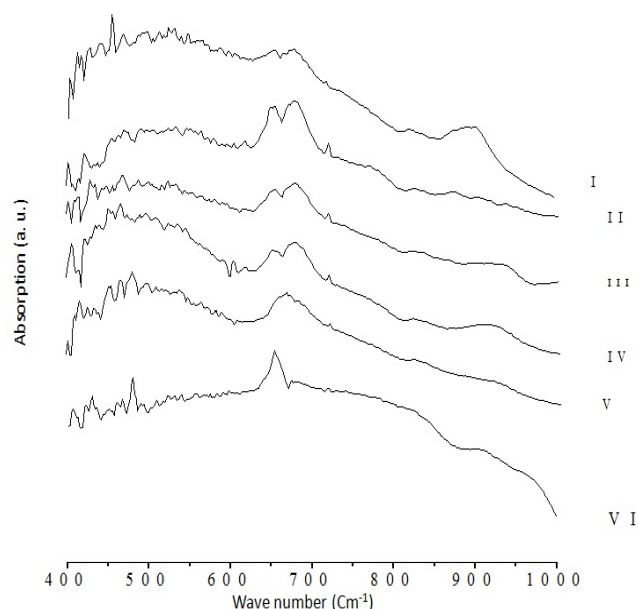


FIG. 1 FTIR SPECTRA OF (I) PEROXOTITANIC ACID AND GEL HEATED AT (II) 110°C (III) 220°C (IV) 330°C (v) 440°C AND (vi) 550°C

The formation of peroxotitanic acid was confirmed from the peak appeared at 900 cm^{-1} which was due to the stretching vibrations of O-O bond in the Ti-O-O-H bond of the peroxotitanic acid as studied by Vasconcelos et al. (2011). The narrow band in the $410\text{--}700\text{ cm}^{-1}$ with maxima at 550°C , the peaks at 480 cm^{-1} and 650 cm^{-1} were assigned to the anatase form of titania as proposed by Bagheri et al. (2013).

The X-ray diffractogram of the gel heated at 550°C has shown in the Fig. 2.

From the JCPDS data (Model-211272 & 181403), it was observed that most of the phases were anatase. The TG and DTG plots of the samples for heating rates 4, 7, and $10^\circ\text{C min}^{-1}$ have been shown in Fig. 3.

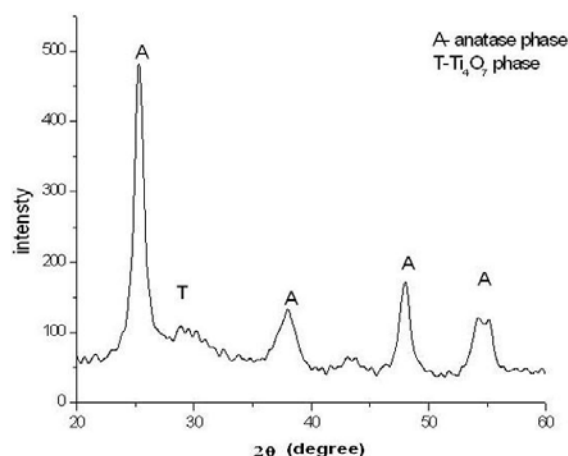
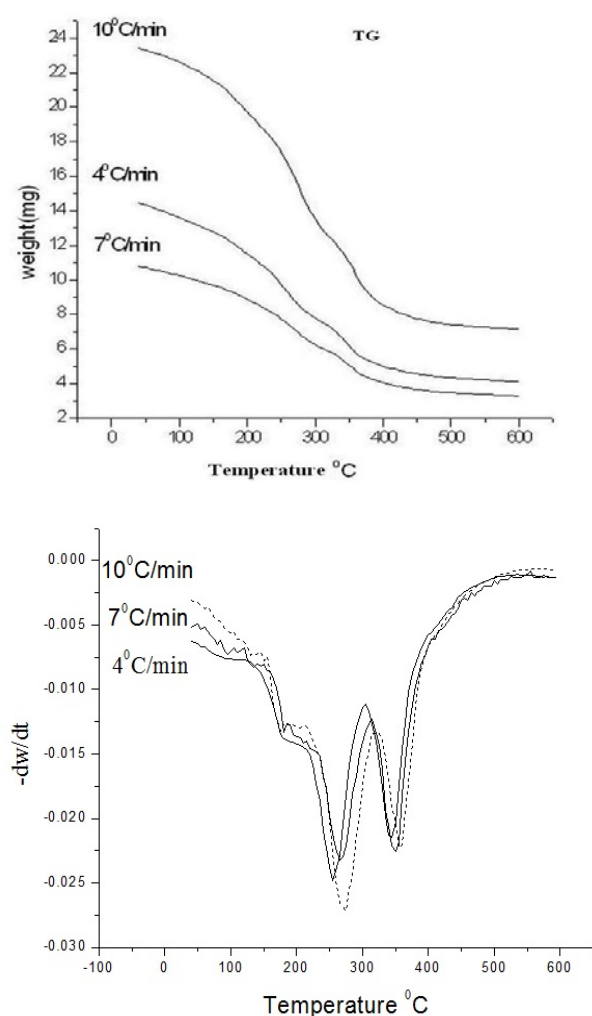
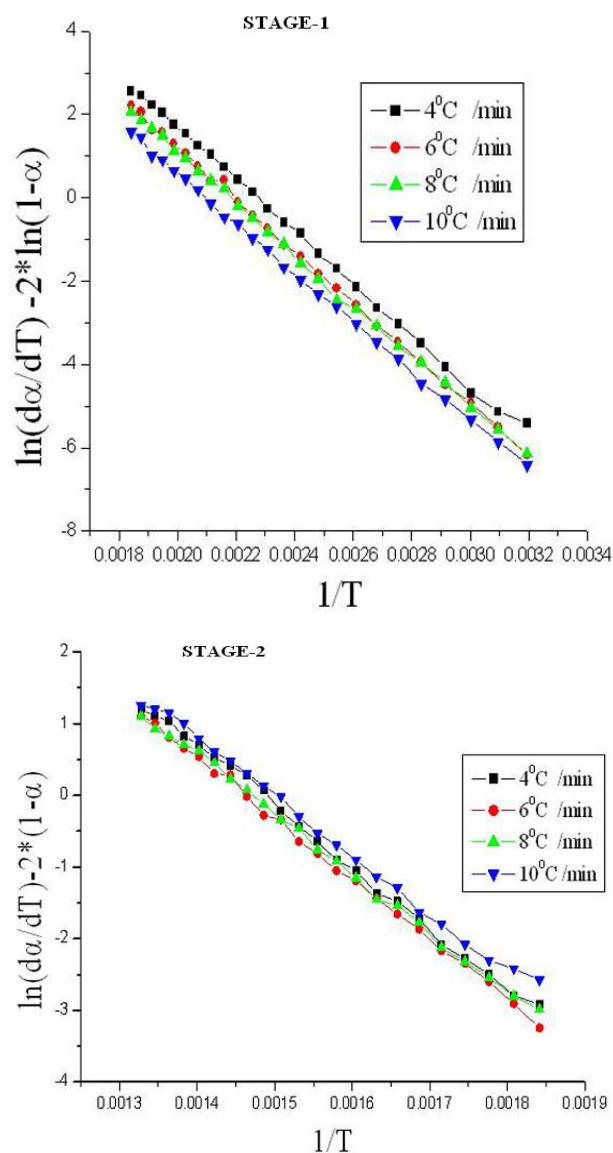


FIG. 2 XRD OF THE GEL HEATED AT 550°C

FIG. 3 TG AND DTG PLOTS OF THE GEL AT HEATING RATES 4, 7, AND 10°C MIN⁻¹

In the TG plot two major changes were observed within the range of 35-310°C and 325-590°C respectively. So we have divided the total dehydration process into two stages and kinetic calculations were performed for the two stages separately. From the TG data, fractional decomposition of the sample was

calculated. In the first stage, the dehydration was complete with a mass loss of 24% on an average, whereas in the second stage almost 8% mass loss was observed. The initial temperature (t_i), peak temperature (t_m) and final temperature (t_f) of dehydration process of both the stages were studied for all the heating rates. It was observed that in both the stages, dehydration temperatures were shifted to higher values with increasing heating rates. This is because at lower heating rates, heat transfer was not so effective and efficient. At higher heating rates, heating of gel particles occurred more gradually leading to an improved and more effective heat transfer to the inner portions and among the particles. The peak temperature was also shifted to higher temperatures with the increasing heating rate as a consequence of increasing rate of volatilization process.

FIG. 4 FRIEDMAN PLOT OF $F(A)=2$ FOR (I) STAGE-1 AND (II) STAGE-2.

Since dehydration of the gel took place in two different stages, so the calculations were performed for both the stages of dehydration separately at all heating rates. During the calculations based on Friedman differential method, it was found that best fit value of n was equal to 2 in both the stages. So it was concluded that dehydration of the gel in both the stages followed second order kinetics. The plots have been shown in Fig. 4.

It implies that the rate of dehydration was controlled not only by the magnitude of hydroxyl group present in the sample but also by the nature of the gel. Now other two parameters (activation energy and pre-exponential factor) of the kinetic triplet were calculated by taking best fit value of $n=2$ for all the three heating rates for both the stages and values found are given in Table-1. The average activation energy for dehydration was found to be lower in stage-1 compared to stage-2. The calculated values of the pre-exponential factor, signifying the fraction of activated species participating in the reaction was found to be much higher in the first stage of dehydration compared to that of the second stage.

TABLE 1 VALUES OF ACTIVATION ENERGY AND FREQUENCY FACTOR BASED ON FRIEDMAN METHOD

Stage	Heating Rate/min	Heating Rate/sec	Activation Energy KJmole ⁻¹	Exponential Factor A x 10 ⁴
			R=8.314	
I	4	0.06666	51.50	8.64
	6	0.1	51.43	7.90
	8	0.13333	50.59	7.62
	10	0.16666	49.27	
Average			50.70	7.09
II	4	0.06666	70.61	1.95
	6	0.1	70.13	2.26
	8	0.13333	68.46	2.36
	10	0.16666	66.92	2.86
Average			69.03	2.36

During calculation based on KAS integral method, F2 mechanism function was found to be the best fit at all three heating rates in case of both the stages. The plots have been shown in Fig. 5.

So it can be confirmed that dehydration of the gel in both stages followed second order based mechanism. With the completion of dehydration at the first stage, the gel framework followed a partial structural collapse, to create more obstruction for the migration of residual water molecules and other volatiles through the structure. The values of activation energy and pre-exponential factor were determined from the slope and intercept of each plot Fig. 6.

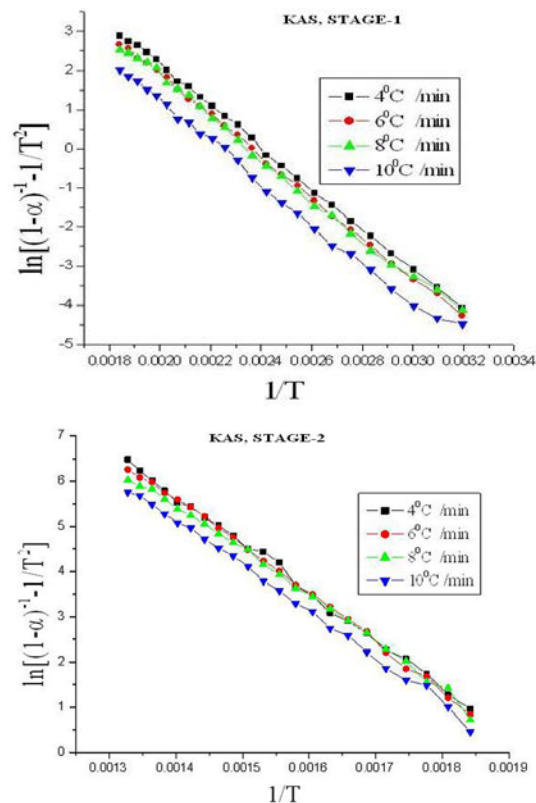


FIG. 5 KAS PLOT OF $G(A)=2$ FOR (I) STAGE-1 AND (II) STAGE-2.

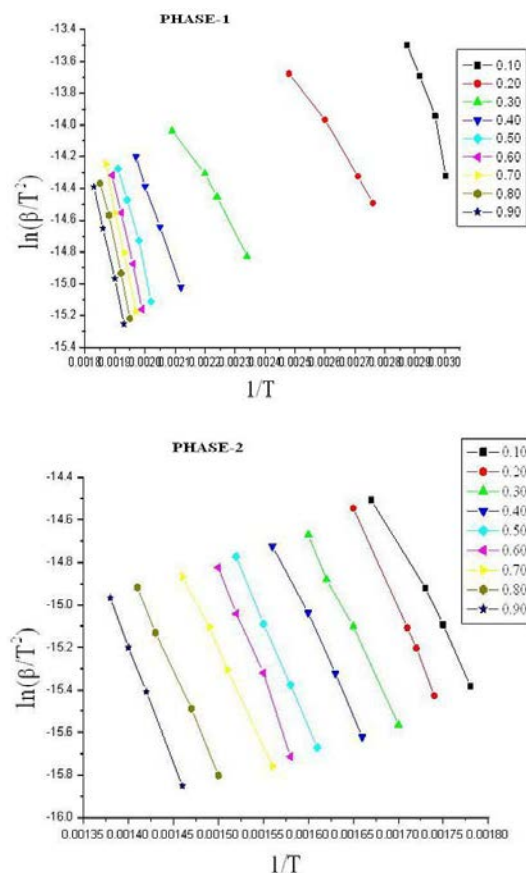


FIG. 6 ISO-CONVERSIONAL PLOTS AT VARIOUS CONVERSION DEGREE OF GEL ACCORDING TO KAS CALCULATION PROCEDURE FOR (I) PHASE-1 (II) PHASE-2 TO DETERMINE ACTIVATION ENERGY AND FREQUENCY FACTOR

using equation-8 were found to be in agreement to those calculated by other method table-2.

TABLE 2 VALUES OF ACTIVATION ENERGY AND FREQUENCY FACTOR BASED ON KAS METHOD.

Stage	Degree of Conversion	Activation Energy KJ mole ⁻¹	Exponential Factor A x 10 ⁴
		R=8.314	
I	0.1	33.68	0.00440
	0.2	24.12	0.00010
	0.3	26.60	0.00009
	0.4	45.44	0.01167
	0.5	60.39	0.49427
	0.6	70.32	6.7798
	0.7	76.34	39.442
	0.8	71.53	16.636
	0.9	70.90	25.908
Average		53.26	9.92
II	0.1	61.23	0.00836
	0.2	81.03	1.1381
	0.3	71.73	0.15202
	0.4	71.21	0.14429
	0.5	80.50	0.8926
	0.6	90.95	8.0802
	0.7	74.63	0.3642
	0.8	82.17	1.4942
	0.9	91.61	12.537
Average		78.34	2.7568

Conclusion

Sol-gel method was used to synthesize titania gel. By using different methods, non-isothermal dehydration kinetics of gel was studied from the thermogravimetric information under dynamic conditions with multiple heating rates. The gel dehydration was observed to take place in two stages and both the stages followed second order kinetics. The activation energy of the second stage was higher than that of the first stage. The calculated values of the pre-exponential factor, signifying the fraction of activated species participating in the reaction was found to be several orders of magnitude in the first stage of dehydration compared to the second stage.

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